RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

PAPER

Benzothiadiazole–an Excellent Acceptor for Indacenodithiophene Based Polymer Solar Cells

Deyu Liu [a,b], Liang Sun [b], Zhengkun Du [b], Manjun Xiao [b], Chuantao Gu [b], Ting Wang [b], Shuguang Wen [b], Mingliang Sun [a*], Renqiang Yang [b*]

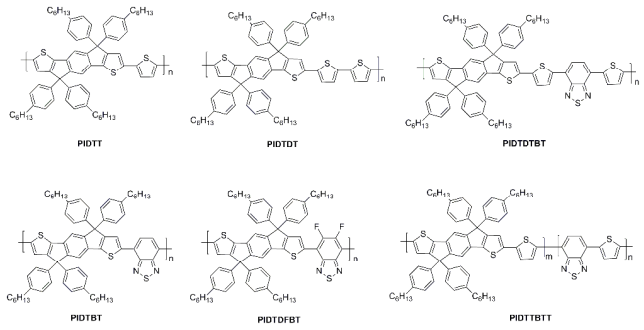
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Two tetradodeoxyphenyl-substituted indacenodithiophene (IDT) based polymer, PIDT3T and PIDTDTBT, were achieved by copolymerizing IDT with terthiophene (3T) or di-2-thienyl-2',1',3'-benzothiadiazole (DTBT). Although these two polymers show significantly different UV-vis absorption spectrum and band gap (2.08 eV and 1.75 eV), the HOMO levels (-5.35 eV and -5.30 eV) of these polymers are almost the same. Polymer solar cells (PSCs) based on polymer with benzothiadiazole (BT) unit show relatively high short-circuit current density (J_{sc}) due to the relatively wide and high photo-electronic response and high hole mobility. Thanks to the four long aryl side chains on IDT, the polymer thin film show amorphous nature, and AFM root-mean-square roughness (RMS) value of the polymer/PCBM blend film is only around 0.3 nm which can contribute to the homogenous bulk heterojunction structures without significant phase seperation. Finally, decent power conversion efficiency (PCE) of 4.52% is achieved by benzothiadiazole based polymer and $PC_{71}BM$ composite. By comparation study, we demonstrate why BT is an excellent acceptor unit for indacenodithiophene-based PSCs.

1. Introduction

Polymer solar cells (PSCs) have attracted increasing interest due to the potential for fabrication of light-weight, large-area, and flexible light-harvesting devices through low-cost solution processing.[1-7] With the prolonged effort, the PCE of PSCs has already exceeded 10%.[8] PSCs usually adopt a bulk-heterojunction (BHJ) structure, where a photoactive layer consists of an interpenetrating network of π-conjugated polymer donors and soluble fullerene or nanocrystal acceptors.[9] Because donor polymer can harvest most of the solar energy, more efforts have been focused on developing conjugated polymers with small band gap and proper energy levels that can be used as a donor material to complement fullerene-based acceptors.[10-14]

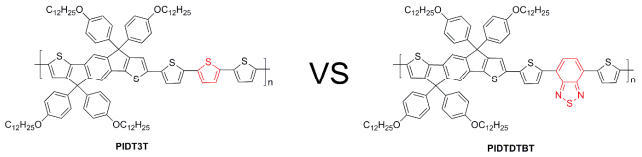
Among different donor materials, indaxenodithiophene (IDT) based conjugated polymers have attracted much attention in optoelectronic devices.[15-17] In IDT, the rigid ring unit could enhance both the degree of conjugation[18] and the co-planarity of the molecular backbones. A series of polymers based on IDT, BT and thiophene have been synthesized (Scheme 1).[19-24,16] The highest PCE reached 7% based the corresponding PSCs.[25] Jen et al. studied several high performance D-A polymers based on IDT and different acceptor units.[26-29] The IDT-based polymers have presented pretty high mobility and the appropriate optical properties, which can facilitate the charge transport simultaneously enhance the absorption of sunlight and subsequently lead to high J_{sc} of PSCs devices.[30] Therefore, both thiophene and BT are promising building blocks for IDT-based polymers. Among these materials, IDT and di-2-thienyl-2',1',3'-benzothiadiazole (DTBT) based high performance polymer solar cells showed PCE up to 6%.[24] In general, the strategy to improve the PCE of solar cells devices is to adjust band gap of polymers.[31,32] Low band gap could enhance the absorption at long wavelengths. However, usually lowering the band gap will lead to the change of the HOMO level, which could reduce V_{oc} of the devices. Increasing J_{sc} and keeping high V_{oc} is a contradiction, but IDT and di-2-thienyl-2',1',3'-benzothiadiazole (DTBT) based polymer solar cells can show high J_{sc} resulting from wide absorption and acceptable V_{oc} resulting from deep HOMO energy level.[24]



Scheme 1. Molecular Structures of IDT-Based Polymers

Typically, the side chain of IDT based polymer was hexyl, and molecular weights (M_n) of polymers (Scheme 1) were exhibited to be in the range of 15-25 K.[19-24,16] Longer side chains on the donor can produce better solubility of the polymer and intermediate oligomers, which may potentially lead to higher

molecular weight.[33] On the other hand, long side chains could reduce the tendency for crystallization to help to obtain the complete noncrystalline materials, which could avoid considering that crystallinity impacts on spectral red shift and mobility in polymer solar cells study. Especially in chemical structure comparation study, long sided chained polymer is favorite.

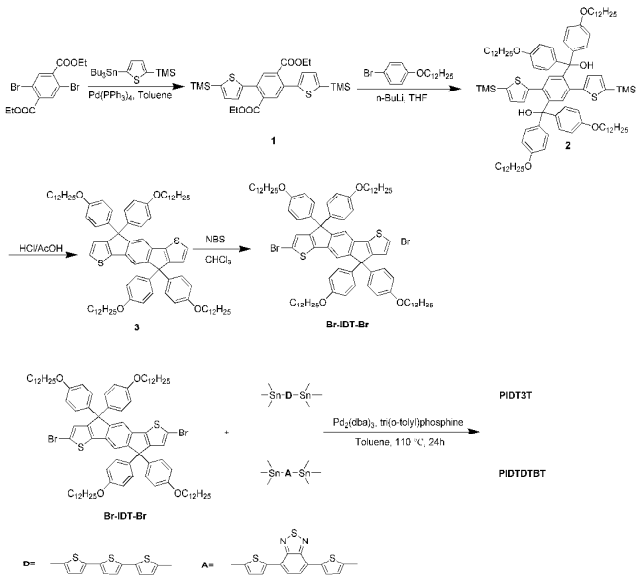


Scheme 2. Molecular Structures of PIDT3T and PIDTDTBT

Here, we synthesized a new tetra-dodeoxyphenyl long chain substituented indacenodithiophene (IDT) derivative and used it as a building unit for polymers. Two IDT-based copolymers PITD3T and PIDTDTBT (Scheme 2) with different building blocks were prepared by Stille polycondensation, and their thermal, optical, electrochemical and photovoltaic properties were investigated. Thanks to the long dodecyl chain, PIDT3T and PIDTDTBT showed high molecular weights (Table 1). Especially, PIDT3T showed one of the highest molecular weights of 61.7 K in IDT based polymers. Compared with PIDT3T polymer, the benzothiadiazole unit in PIDTDTBT polymer was introduced to lower the band gap and increase the absorption. Fortunately, the introduction of BT could lower the band gap and increase J_{sc} effectively, while the HOMO level did not changed. Thanks to the amorphous nature of these polymers, the comparison of two polymers is completely due to difference of the thiophene and the BT in the middle of other units. In this paper, by comparation study we demonstrate why BT is an excellent acceptor unit for indacenodithiophene-based PSCs.

2. Results and discussion

2.1. Synthesis of monomers and polymers



Scheme 3. Synthetic routes of the IDT monomer and the IDT-based copolymers

Table 1 Molecular weights and thermal properties of PIDT3T and PIDDTBT

polymers	M_n	M_w	PDI	T_d (°C)
PIDT3T	61.7 K	62.6 K	1.01	374
PIDTDTBT	35.1 K	44.3 K	1.26	422

The synthetic routes of the monomer (IDT) and the copolymer are depicted in Scheme 3. The synthesis of the indaxenodithiophene (IDT) was generally based on the previous literature.[34] The TMS groups on compound 1 (Scheme 3) were introduced to facilitate the later intramolecular cyclization reactions. Two polymers, PIDT3T and PIDTDTBT, were synthesized by using palladium-catalyzed Stille coupling copolymerization of IDT with 3T and DTBT.[35] The structures of two polymers were confirmed by ^{1}H NMR spectroscopy. Both polymers showed good solubility in common organic solvents, such as chloroform, toluene and chlorobenzene, due to the four dodeoxyphenyl side chains in the IDT repeat unit. The number-average molecular weight (M_n) and polydispersity index (PDI) were measured by gel permeation chromatography (GPC) using THF as the eluant and polystyrenes as the internal standards, and the results were listed in Table 1. The M_n of PIDT3T and PIDTDTBT are 61.7 K and 35.1 K, respectively. Molecular weights of the copolymers are relatively high, probably due to the good solubility of IDT monomer with long side chains.

2.2. Thermal analysis

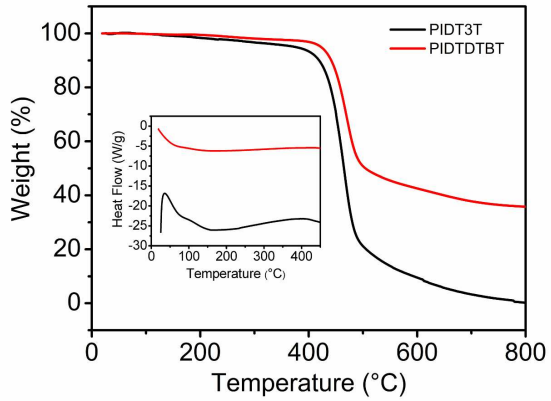


Fig. 1 TGA of the polymers with a heating rate of 10 °C/min under an inert atmosphere (Inset: DSC thermogram of the polymers)

The thermal properties of the polymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), as shown Fig. 1. DSC thermogram didn't show apparent thermal transitions for PIDT3T and PIDTDTBT polymer, implying their amorphous nature. The TGA analysis reveals that the onset temperature with 5% weight-loss (T_d) of PIDT3T and PIDTDTBT are 374 °C and 422 °C, respectively. DTBT unit has higher thermal stability than 3T unit,[36,37] which results in higher thermal stability of PIDTDTBT polymer. This indicates that the thermal stability of the polymers is good enough for PSCs applications.

2.3. Optical properties

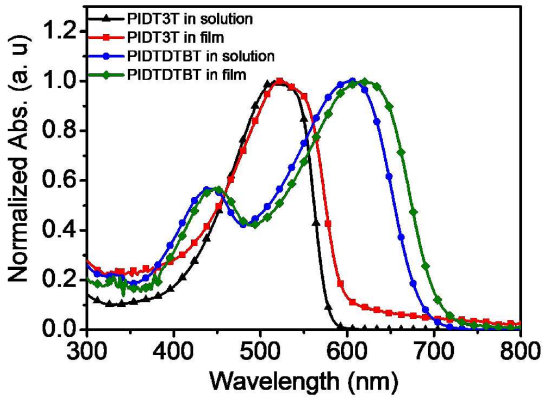


Fig. 2 Normalized absorption spectra of the PIDT3T and PIDTDTBT in chloroform solution and in thin film

The UV-vis absorption spectra of PIDT3T and PIDTDTBT in chloroform solution and in thin film are shown in Fig. 2, respectively, and the corresponding absorption properties are summarized in Table 2. PIDT3T exhibited one absorption band due to the π-π* transition with the absorption maximum at 516 nm. PIDTDTBT exhibited two absorption bands due to the π-π* transition and the intramolecular charge transfer with the absorption maximum at 450 nm and 606 nm in chloroform solution. In the thin film, both polymers exhibit a red-shift in the absorption maximum and onset, which is attributed to solid state packing effects. Compared the absorption in thin film with that in solution, PIDTDTBT polymer exhibits a greater red-shift compared to PIDT3T, which is attributed to more effective π-π stacking.[38,39] PIDTDTBT polymer shows more planar polymer structure and packs better than PIDT3T. The optical band gaps (E_g^{opt}) of PIDT3T and PIDTDTBT were estimated to be 2.08 eV and 1.75 eV according to E_g^{opt}=1240/λ. Due to the introduction of BT unit, the band gap of PIDTDTBT was obviously lowered compared with PIDT3T. The lower band gap of PIDTDTBT should be beneficial to its application as donor material in PSCs.

2.4. Electrochemical properties

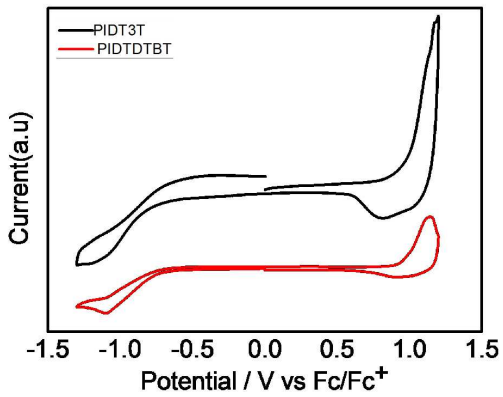


Fig. 3 Cyclic voltammogram of PIDT3T and PIDTDTBT

Table 2 Optical and electrochemical properties of the polymers

polymer	λ_{max} solution (nm)	λ_{max} film (nm)	E_g^{opt} Film (eV)	E_g^{cv} (eV)	HOMO (eV)	LUMO (eV)
PIDT3T	516	522	2.08	1.8	-5.35	-3.55
PIDTDTBT	606	622	1.75	1.6	-5.30	-3.70

The electrochemical cyclic voltammetry (CV) was performed for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymers.[40] Fig. 3 shows the cyclic voltammogram (CV) properties of the polymers. A three electrode cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode has been used. The potentials were internally calibrated using the Fc/Fc^+ redox couple. The redox potential of the Fc/Fc^+ internal reference is found to be 0.43 V vs. SCE. According to the empirical equation,

$$HOMO = -(E_{ox}+4.4)\ (eV)$$

$$LUMO = -(E_{re}+4.4)\ (eV)$$

The results of the electrochemical properties are listed in Table 2. Compared with PIDT3T, the LUMO energy levels of PIDTDTBT decreased significantly due to the electron-withdrawing ability of the acceptor unit, but the HOMO energy levels of the polymer changed little, which is possibly due to similar oxidation potential of 3T and DTBT. These two polymers show deep HOMO energy levels (~-5.3 eV), which is desirable for good stability in the air and high open circuit voltage (V_{oc}) in PSCs.

2.5. Photovoltaic properties

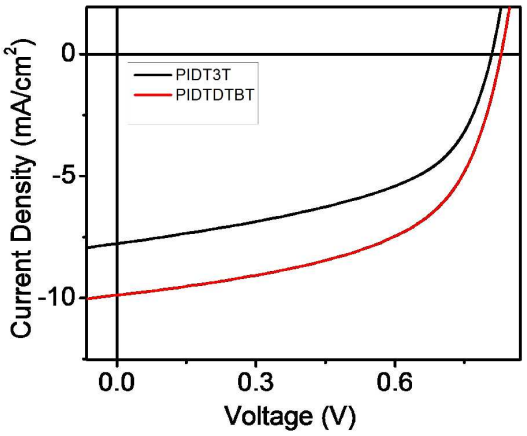


Fig. 4 J-V curves of the PSCs based on the blend of PIDT3T or PIDTDTBT/$PC_{71}BM$ under the illumination of AM 1.5G, 100 $mWcm^{-2}$

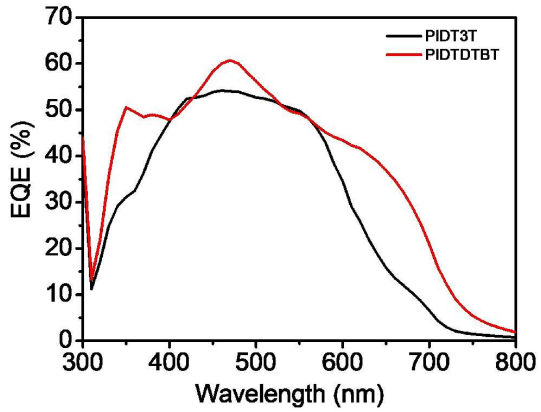


Fig. 5 EQE of curves of the PSCs based on the blend of PIDT3T or PIDTDTBT/$PC_{71}BM$

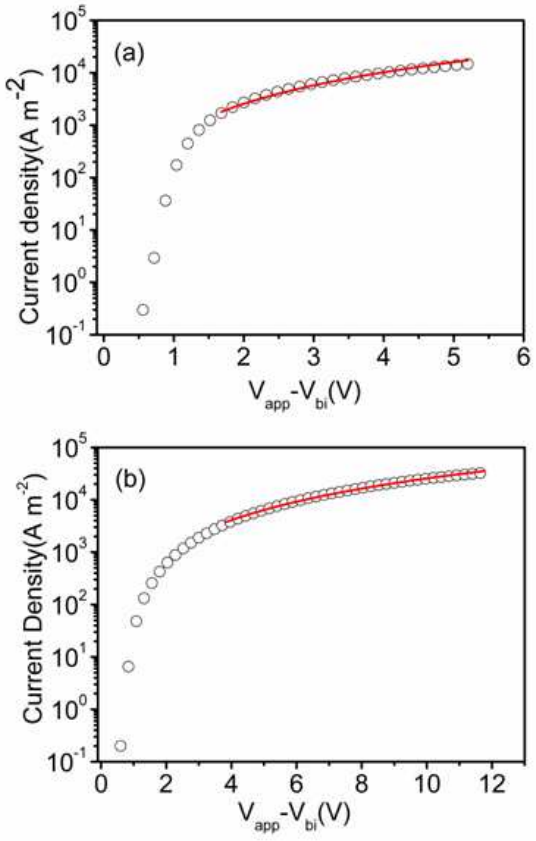


Fig. 6 Current density (J)-voltage (V) curves for PIDT3T based device (a) and PIDTDTBT based device (b) (the symbols are experimental data for transport of hole, and the red line is fitted according to the space-charge-limited-current model)

To investigate and compare the photovoltaic properties of the polymers, bulk heterojunction PSCs devices with a configuration of ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Ca/Al were fabricated by the method of solution processing as our previous work.[41-43] And then, we further optimized the device performances using $PC_{71}BM$ acceptor with device configuration ITO/PEDOT:PSS/polymers:$PC_{71}BM$ (1:3)/Ca/Al. Fig. 4 exhibits the J-V curves of the PSCs under illumination of AM 1.5G, 100 mWcm^{-2}. Table 3 summarized the detailed device performances. Finally, the best solar cell obtained from PIDT3T:$PC_{71}BM$ (1:3) showed a PCE of 3.26% with an V_{oc} of 0.81 V, a J_{sc} of 7.75 mAcm^{-2}, and a FF of 51.93% and PIDTDTBT showed a PCE of 4.52% with an V_{oc} of 0.83 V, a J_{sc} of 9.85 mAcm^{-2}, and a FF of 53.26% at the same condition. The V_{oc} of two polymers based PSCs devices was almost the same due to the similar HOMO level. Compared to the PIDT3T, PIDTDTBT showed higher J_{sc} value, which may be originated from the relatively lower band gap and stronger π-π stacking interaction. The external quantum efficiency (EQE) curves of the devices based on PIDT3T:$PC_{71}BM$ and PIDTDTBT:$PC_{71}BM$ (1:3) are shown in Fig. 5. The EQE value of PIDTDTBT is higher than that of PIDT3T in most parts of spectra (320 nm-700 nm) and the maximum value reaches 61%. It indicates that PIDTDTBT has good photo response among the absorption range. The calculated current density from the EQE measurement were 7.66 and 9.74 mAcm^{-2}, respectively for PIDT3T and PIDTDTBT, which agree well with the J_{sc} (7.75mAcm^{-2} for PIDT3T and 9.85 mAcm^{-2} for PIDTDTBT) obtained from the J-V measurements.

Mobility measurements via space charge limited current (SCLC) method [40] disclose a hole mobility of 2.35×10^{-4} $cm^2V^{-1}s^{-1}$ for the PIDTDTBT:$PC_{71}BM$ device, higher than that of the PIDT3T:$PC_{71}BM$ device (1.31×10^{-4} $cm^2V^{-1}s^{-1}$). This could be a potential reason that PIDTDTBT:$PC_{71}BM$ device exhibits larger J_{SC} and FF than PIDT3T:$PC_{71}BM$ device.

Table 3 Solar cells devices performance of PIDT3T and PIDTDTBT

Polymers/Acceptor	V_{oc}/V	J_{sc}/mAcm^{-2}	FF/(%)	PCE/(%)
PIDT3T/$PC_{61}BM$	0.81	5.06	49.7	2.03
PIDT3T/$PC_{71}BM$	0.81	7.75	51.93	3.26
PIDTDTBT/$PC_{61}BM$	0.85	7.13	58.48	3.56
PIDTDTBT/$PC_{71}BM$	0.83	9.85	55.26	4.52

The active layers were annealed at 150 ° C for 10 min.

2.6. Morphological Characterization

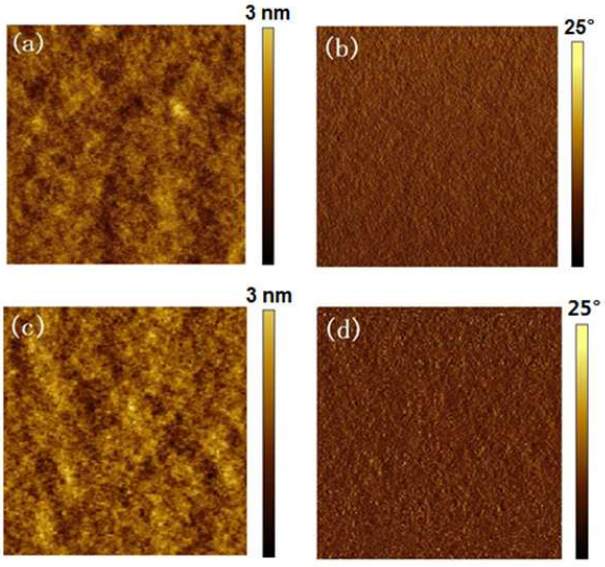


Fig. 7 AFM height (a) and phase (b) images of the PIDT3T:$PC_{71}BM$ (1:3) blend films annealed at 150 °C; AFM height (c) and phase (d) images of the

PIDTDTBT:$PC_{71}BM$ (1:3) blend films annealed at 150 °C (All the images are 4 μm×4 μm)

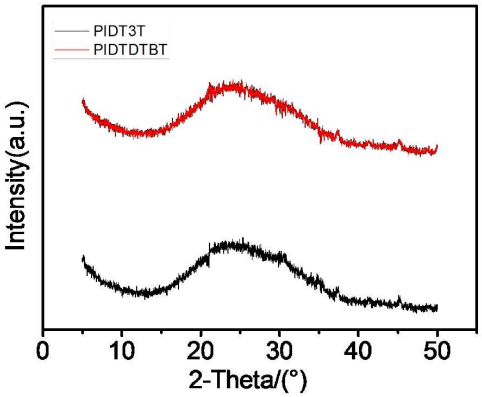


Fig. 8 X-ray diffraction (XRD) pattern of the PIDT3T and the PIDTDTBT

Atomic force microscopy (AFM) was used to investigate the morphology of the two polymers: $PC_{71}BM$ blend films annealed at 150 °C. The height images and phase images of the blends are shown in Fig. 7. The blend films of PIDT3T and PIDTDTBT with $PC_{71}BM$ showed surface roughness with root-mean-square (RMS) of 0.343 nm and 0.328 nm, respectively. Although with a smooth surface morphology of the active layer, the device based on PIDT3T has a lower J_{sc} value than PIDTDTBT which can be attributed to its lower EQE value. The crystallinity of the polymer films was investigated using XRD pattern, as shown in Fig. 8. There are no peaks observed for these polymers in XRD test, indicating their amorphous nature.

3. Conclusions

We have successfully synthesized two indacenodithiophene-based polymers PIDT3T and PIDTDTBT. Thanks to the long side chain, the polymers show high (up to 6.0K) molecule weight with narrow PDI and amorphous nature (no crystalization). Although these two polymers show significantly different UV-vis absorption spectrum and band gap (2.08 eV and 1.75 eV), the HOMO levels (-5.35 eV and -5.30 eV) are almost the same. PSCs based on these two materials show almost the same V_{oc} (around 0.8 V) due to the same HOMO level. PSCs based on PIDTDTBT with benzothiadiazole unit show relatively high J_{sc} and FF due to the relatively wide and high photo-electronic response and high hole mobility. Our comparation study shows that BT is a good acceptor unit in IDT polymer backbone which does broad absorption to increase J_{sc} of PSCs devices without lowing V_{oc} of the device due to proper HOMO levels.

4. Experimental

4.1. Materials

All chemicals, unless otherwise specified, were commercial grade and used as received. Toluene and THF were freshly distilled from sodium and benzophenone ketyl under nitrogen prior to use. 5-(Trimethylsilyl)-2-(tri-n-butylstannyl)thiophene, 4-dodeoxy-1-bromobenene, 2,5”-bis(trimethylstannyl)-5,2’,5’,2”-terthiophene were synthesized as reported in the literature.[44-47]

4.2. Instruments and measurements

Nuclear magnetic resonance (NMR) spectra were taken on a Bruker AVANCE-III 600 Spectrometer. High resolution mass spectra (MS) were recorded under APCI mode on a Bruker Maxis UHRTOF spectrometer. All GPC analyses were made using tetrahydrofuran (THF) as eluant and polystyrene standard as reference. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements were performed on STA-409 at a heating rate of 10 °Cmin^{-1}. UV-vis absorption spectrum was measured with a Hitachi U-4100 spectrophotometer. The organic molecule films on quartz used for absorption spectral measurement were prepared by spin-coating their chloroform solutions. Cyclic voltammetry (CV) was performed using a CHI660D electrochemical workstation with a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode at a scan rate of 100 mVs^{-1}. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in acetonitrile was used as the supporting electrolyte. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM) on an Agilent 5400 working at the tapping mode. X-ray diffraction (XRD) pattern were recorded on a Bruker D8 Advance.

4.3. Fabrication and characterization of organic solar cells

Photovoltaic devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates with a layered structure of ITO/PEDOT:PSS/donor: acceptor/Ca(10 nm)/Al(100 nm). The ITO coated glass substrates were cleaned in ultrasonic bath in acetone, toluene, methanol and isopropyl alcohol sequentially. And then, oxygen plasma treatment was made for 20 min, spin-coated with PEDOT:PSS at 5000 rpm, and dried under argon for 20 min at 120 °C. The photosensitive layer was prepared by spin-coating a blend solution of the polymers and $PC_{61}BM$ （$PC_{71}BM$） with a weight ratio of 1:3 in deoxygenated anhydrous *o*-dichlorobenzene at 2000 rpm on the ITO/PEDOT:PSS substrate and then annealed at 150 °C for 10 min in a glove box. The thickness of active layer films measured by a Dektak 150 profilometer is around 100 nm. Finally, Ca (10 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of ~2×10^{-4} Pa on top of active layer. The photovoltaic performance was measured under illumination at 100 $mWcm^{-2}$ AM 1.5G irradiation using a Xe arc lamp in an argon atmosphere (<0.1 ppm H_2O and O_2), and the current density-voltage (J-V) curves was obtained by Keithley 2400. The external quantum efficiency (EQE) was obtained by a source meter, silicon photodiode and a computer-controlled light source-monochromator-lock-in system.

4.4. Synthesis

Diethyl-1,4-Bis(5-trimethylsilylthiophen-2-yl)-2,5-benzene-dicarbonate (1)

Diethyl-2,5-dibromoterephthalate (3.04 g, 8 mmol), 5-(trimethylsilyl)-2-(tri-n-butylstannyl)-thiophene (8.91 g, 20 mmol) and $Pd(PPh_3)_4$ (462 mg, 0.4 mmol) were mixed in toluene (60 ml) under nitrogen atmosphere. The mixture was heated to reflux for 48 h. After cooled to room temperature, it was poured into water and extracted with ethyl acetate. The combined extracts were

dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel, eluting with petroleum ether and ethyl acetate (v/v, 10/1) to give (1) as a white solid (1.29 g, 31%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 2H), 7.18 (d, J = 3.4 Hz, 2H), 7.14 (d, J = 3.4 Hz, 2H), 4,21 (q, J =7.1 Hz, 4H) 1.13 (t, J = 7.1 Hz, 6H), 0.34 (s, 18H).

4,9-Dihydro-4,4,9,9-(p-dodeoxyphenyl)-s-indaceno[1,2-b:5,6-b]dithiophene (3)

To a solution of 4-dodeoxy-1-bromobenene (6.14 g, 18 mmol) in THF (10 ml) at -78 °C, n-BuLi (11.25 ml, 18 mmol, 1.6 M in hexane) was added, and the mixture was keep at -78 °C for 1 h, then a solution of compound (1) (1.06 g, 2 mmol) in THF (5 ml) was added slowly. The mixture was stirred at room temperature overnight and then poured into water and extracted with chloroform. The combined organic extracts were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The resulting solid was washed with hexanes to give (2) as a white solid crude product. The white product was then directly dissolved in acetic acid (25 ml) and 1 ml of concentrated hydrochloric was added to the solution. The mixture was stirred at 80 °C for 2 h. After pouring into water, the mixture was extracted with chloroform. The combined organic extracts were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The resulting solid was washed with water, an aqueous sodium carbonate solution, and methanol to give (3) as a yellow solid (1.28 g, 51%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.38 (s, 2H), 7.23 (d, J = 4.9 Hz, 2H), 7.14 (dd, J = 6.9 Hz, 8H), 6.96 (d, J = 4.9 Hz, 2H), 6.76 (d, J = 8.4 Hz, 8H), 3.89 (t, J = 6.5 Hz, 8H), 1.73 (m, 8H), 1.41(m, 8H), 1.35-1.20 (m, 64H), 0.87 (t, J = 7.0 Hz, 12H).

2,7-Dibromo-4,9-dihydro-4,4,9,9-(p-dodeoxyphenyl)-s-indaceno[1,2-b:5,6-b']dithiophene (Br-IDT-Br).

To a solution of 3 (1.27 g, 1 mmol) dissolved in chloroform (25 ml), NBS was added (391 mg, 2.2 mmol). The mixture was stirred under dark at room temperature overnight and extracted with chloroform and water. The combined organic extracts were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica, eluting with petroleum ether to give the monomer as a yellow solid (1.35 g, 92%). ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.28 (s, 2H), 7.10 (d, J = 8.8 Hz, 8H), 6.96 (s, 2H), 6.77 (d, J = 8.9 Hz, 8H), 3.90 (t, J = 6.5 Hz, 8H), 1.74 (m, 8H), 1.42 (m, 8H), 1.35-1.20 (m, 64H), 0.88 (t, J = 7.0 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 158.20, 155.13, 152.86, 141.14, 135.89, 134.90, 128.91, 125.92, 117.05, 114.30, 113.81, 67.96, 62.71, 31.92, 29.66, 29.63, 29.60, 29.58, 29.40, 29.35, 29.29, 26.08, 22.69, 14.13. MS （MALDI-TOF）：cacld for $C_{88}H_{120}Br_2O_4S_2$ $[M]^+$，1464.6974；found：1464.7075.

Synthesis of PIDT3T

To a 25 ml flask, 2,7-dibromo-4,9-dihydro-4,4,9,9-(p-dodeoxyphenyl)-s-indaceno[1,2-b:5,6-b']dithiophene (254 mg, 0.2 mmol), 2,5"-bis(trimethylstannyl)-5,2',5',2"-terthiophene (115 mg, 0.2 mmol), $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol), and tri(o-tolyl)phosphine (11 mg, 0.036 mmol) were added under nitrogen protection. After the addition of toluene (5 ml), the mixture was heated to 110 °C and maintained at the same temperature for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and purified by column chromatography over silica using chloroform as the eluant. After removing the solvent, the resulting red solid was dissolved into a small amount of chloroform and then poured methanol again. The product was collected and dried overnight under vacuum with the yield 81% for PIDT3T as a red solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.34 (s, 2H), 7.18-6.80 (m, 24H), 3.91 (br, 8H), 1.75 (br, 8H), 1.42 (br, 8H), 1.35-1.20 (m, 64H), 0.87 (t, J = 7.0 Hz, 12H). GPC (THF at room temp.): M_n=61.7 K, M_w=62.6 K, PDI= 1.01.

Synthesis of PIDTDTBT

To a 25 ml flask, 2,7-dibromo-4,9-dihydro-4,4,9,9-(p-dodeoxyphenyl)-s-indaceno[1,2-b:5,6-b']dithiophene (254 mg, 0.2 mmol), 4,7-di(2-trimethylstannylthiophen-5-yl)-2,1,3-benzothiadiazole (125 mg, 0.2 mmol), $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol) and tri(o-tolyl)phosphine (11 mg, 0.036 mmol) were added under nitrogen protection. The other procedures are just as PIDT3T. The product was obtained with the yield 63% for PIDTDTBT as a dark-blue solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.01-7.84 (m, 4H), 7.38 (br, 2H), 7.23-6.81 (m, 20H), 3.92 (br, 8H), 1.75 (br, 8H), 1.43 (br, 8H), 1.37-1.20 (m, 64H), 0.86 (t, J = 7.0 Hz, 12H). GPC (THF at room temp.): M_n=35.1 K, M_w=44.3 K, PDI= 1.26.

Acknowledgments

The authors are deeply grateful to the National Natural Science Foundation of China (Project no. 21274134, 21202181, 51303197 and 51173199), New Century Excellent Talents in University (NCET-11-0473), and Qingdao Municipal Science and Technology Program (13-1-4-200-jch) for financial support.

Notes

[a] *Institute of Material Science and Engineering, Ocean University of China, Qingdao 266100, People's Republic of China. Fax: 86-532-66781927; Tel: 86-532-66781690; E-mail: mlsun@ouc.edu.cn*

[b] *CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, People's Republic of China. Fax: 86-532-80662778; Tel: 86-532-80662700; E-mail: yangrq@qibebt.ac.cn*

References

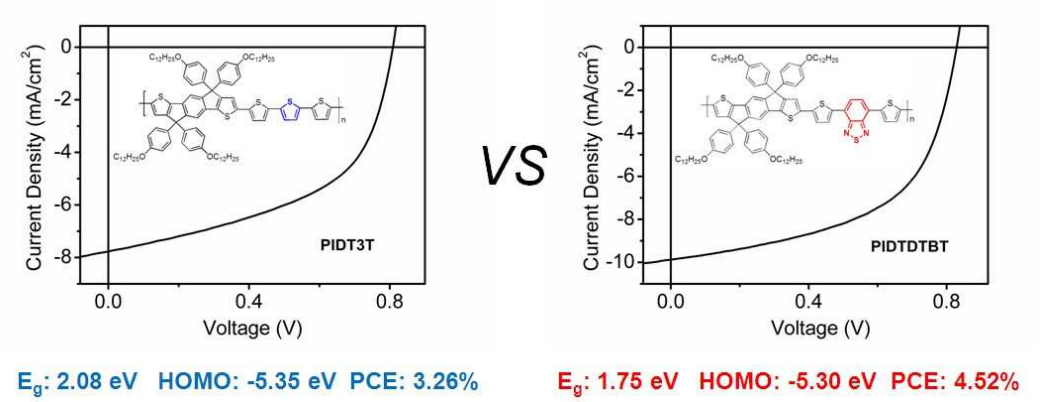
1. Barbec, C. J., *Solar Energy Materials and Solar Cells*. 2004, **83**, 273-292.
2. Chen, H. C.; Chen, Y. H.; Liu, C. C.; Chien, Y. C.; Chou, S. W.; Chou, P. T., *Chemistry of Materials.* 2012, **24**, 4766-4772.
3. Zhang, M.; Gu, Y.; Guo, X.; Liu, F.; Zhang, S.; Huo, L.; Russell, T. P.; Hou, J., *Advanced materials*. 2013, **25**, 4944-4949.
4. Zhang, M.; Guo, X.; Ma, W.; Zhang, S.; Huo, L.; Ade, H.; Hou, J., *Advanced materials*. 2014, **26**, 2089-2095.
5. Yuan, J.; Zhai, Z.; Dong, H.; Li, J.; Jiang, Z.; Li, Y.; Ma, W., *Advanced Functional Materials*. 2013, **23**, 885-892.
6. Scharber, M. C.; Sariciftci, N. S., *Progress in polymer science*. 2013, **38**, 1929-1940.
7. Liu, Q.; Bao, X. C.; Wen, S. G.; Du, Z. K.; Han, L. L.; Zhu, D. Q.; Chen, Y. H.; Sun, M. L.; Yang, R. Q., *Polymer Chemistry*. 2014, **5**, 2076-2082.

8. You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C. C.; Gao, J.; Li, G.; Yang, Y., *Nature Communications*. 2013, **4**, 1446.
9. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger. A. J., *Science*. 1995, **270**,1789-1791.
10. Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K., *Chemical Reviews*. 2010, **110**, 6817-6855.
11. Cheng, Y. J.;Yang, S. H.; Hsu, C. S., *Chemical Reviews*. 2009, **109**, 5868-5923.
12. Li, Y.; Zou, Y., *Advanced Materials*. 2008, **20**, 2952-2958.
13. Bundgaard, E.; Krebs, F., *Solar Energy Materials and Solar Cells.* 2007, **91**, 954-985.
14. Roncali, J., *Chemical Reviews.* 1997, **97**, 173-206.
15. Chen, Y.; Yu, C.; Fan, Y.; Hung, L.; Chen, C.; Ting, C., *Chemical Communications*. 2010, **46**, 6503-6505.
16. Zhang, Y.; Zou, J.; Yip, H. L.; Chen, K. S.; Zeigler, D. F.; Sun, Y.; Jen, A. K. Y., *Chemistry of Materials*. 2011, **23**, 2289-2291.
17. Zhang, W. M.; Smith, J.; Watkins, S. E.; Gysel, R.; McGehee, M.; Salleo, A.; Kirkpatrick, J.; Ashraf, S.; Anthopoulos, T.; Heeney, M.; McCulloch, I., *Journal of the American Chemical Society*. 2010, **132**, 11437-11439.
18. Ando, S.; Nishida, J.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y., *Journal of the American Chemical Society*. 2005, **127**, 5336-5337.
19. Zhang, M.; Guo, X.; Wang, X.; Wang, H.; Li, Y., *Chemistry of Materials*. 2011, **23**, 4264-4270;
20. Chen, Y. C.; Yu, C. Y.; Fan, Y. L.; Hung, L. I.; Chen, C. P.; Ting, C., *Chemical Communications*. 2010, **46**, 6503−6505.
21. Chen, C. P.; Chen, Y. C.; Yu, C. Y., *Polymer Chemistry*. 2013, **4**, 1161-1166.
22. Ashraf, R. S.; Schroeder, B. C.; Bronstein, H. A.; Huang, Z.; Thomas, S.; Kline, R. J.; Brabec, C. J.; Rannou, P.; Anthopoulos, T. D.; Durrant, J. R.; McCulloch, I., *Advanced Materials.* 2013, **25**, 2029-2034;
23. Chan, S. H.; Chen, C. P.; Chao, T. C.; Ting, C.; Lin, C. S.; Ko, B. T., *Macromolecules*. 2008, **41**, 5519-5526.
24. Chen, K. S.; Zhang, Y.; Yip, H. L.; Sun, Y.; Davies, J. A.; Ting, C.; Chen, C. P.; Jen, A. K. Y., *Organic Electronics.* 2011, **12**, 794-801.
25. Xu, Y. X.; Chueh, C. C.; Yip, H. L.; Ding, F. Z.; Li, Y. X.; Li, C. Z.; Li, X.; Chen, W. C.; Jen, A. K., *Advanced Materials*. 2012, **24**, 6356-6541.
26. Zhang, Y.; Zou, J.; Yip, H.-L.; Chen, K.-S.; Davies, J. A.; Sun, Y.; Jen, A. K. Y., *Macromolecules.* 2011, **44**, 4752-4758.
27. Sun, Y.; Chien, S. C.; Yip, H. L.; Zhang, Y.; Chen, K. S.; Zeigler, D. F.; Chen, F. C.; Lin, B.; Jen, A. K. Y., *Journal of Materials Chemistry*. 2011, **21**, 13247−13255.
28. Zhang, Y.; Chien, S. C.; Chen, K. S.; Yip, H. L.; Sun, Y.; Davies, J. A.; Chen, F. C.; Jen, A. K. Y., *Chemical Communications.* 2011, **47**, 11026−11028.
29. Xu, Y. X.; Chueh, C. C.; Yip, H. L.; Ding, F. Z.; Li, Y. X.; Li, C. Z.; Li, X.; Chen, W. C.; Jen, A. K., *Advanced Materials*. 2012, **24**, 6356-6361.
30. Zhang, W.; Smith, J.; Watkins, S. E.; Gysel, R.; McGehee, M.; Salleo, A.; Kirkpatrick, J.; Ashraf, S.; Anthopoulos, T.; Heeney, M.; McCulloch, I., *Journal of the American Chemical Societ*y. 2010, **132**, 11437−11439.
31. Huo, L.; Guo, X.; Zhang, S.; Li, Y.; Hou, J. H., *Macromolecules*. 2011, **44**, 4035-4037.
32. He, Z.; Zhong, C.; Huang, X.; Wong, W.Y.; Wu, H.; Chen, L.; Su, S.; Cao, Y., *Advanced Materials.* 2011, **23**, 4636-4643.
33. Mei, J.; Bao, Z., *Chemistry of Materials*. 2014, **26**, 604-615.
34. Wong, K. T.; Chao, T. C.; Chi, L. C.; Chu, Y. Y.; Balaiah, A.; Chiu, S. F.; Liu, Y. H.; Wang, Y., *Organic Letters.* 2006, **8**, 5033-5036.
35. Bao, Z. N.; Chan, W. K.; Yu. L. P., *Journal of the American Chemical Society*. 1995, **117**, 12426-12435.
36. Kitamura, C.; Tanaka, S.; Yamashita, Y., *Chemistry of Materials*. 1996, **8**, 570-578;
37. Beny, J. P.; Dhawan, S. N.; kagan, J.; Sundlass, S., *Journal of Organic Chemistry.*1982, **47**, 2201-2204.
38. Duan, C.; Chen, K. S.; Huang, F.; Yip, H. L.; Liu, S.; Zhang, J.; Jen, A. K. Y.; Cao, Y., *Chemistry of Materials*. 2010, **22**, 6444-6452;
39. Peng, Q.; Liu, X.; Su, D.; Fu, G.; Xu, J.; Dai, L., *Advanced Materials*. 2011, **23**, 4554-4558.
40. Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J., *Synthetic Metals*. 1999, **99**, 243-248.
41. Sun, M. L.; Wang, L.; Xia, Y. J.; Du, B.; Liu, R. S.; Cao, Y., *Acta Polymerica Sinica.* 2007, **10**, 952-958.
42. Sun, M. L.; Wang, L.; Zhu, X. H.; Du, B.; Liu, R. S.; Yang, W.; Cao, Y., *Solar Energy Materials and Solar Cells*. 2007, 91, 1681-1687.
43. Sun, M. L.; Wang, L.; Du, B.; Liu, R. S.; Cao, Y., *Synthetic Metals*. 2008, 1**58**, 125-129.
44. Price, S. C.; Stuart, A. C.; You, W., *Macromolecules*. 2010, **43**, 4609-4612.
45. Liebeakind, L. S.; Wang, J. Y., *Journal of Organic Chemistry.* 1993, **58**, 3550-3556.
46. Kraft, A.; Grimsdale, A. C.; Holmes, A. B., *Angewandte Chemie (International ed. in English).* 1998, **37**, 402-428.
47. Liu, X. M.; Lin, T. T.; Huang, J. C.; Hao, X. T.; Ong, K. S.; He, C. B., *Macromolecules*. 2005, **38**, 4157-4168.

Graphical and textual abstract

Indacenodithiophene is copolymerized with di-2-thienyl-2',1',3'-benzothiadiazole or terthiophene.

The reason why benzothiadiazole based polymer show high PCE is discussed.



E_g: 2.08 eV HOMO: -5.35 eV PCE: 3.26%

E_g: 1.75 eV HOMO: -5.30 eV PCE: 4.52%